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(57) Abstract

The invention relates to hyperbranched polyesters, to a process for the manufacture thereof, to their use in unsaturated polyester preparations and to curable resins comprising hyperbranched polyesters. The process for the manufacture of hyperbranched polyesters comprises the following steps: a) reacting a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably free carboxyl groups, with a polyol with 2 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, in the presence of an amine, the amount of ahnydride being at least 1 mol of anhydride per hydroxyl group of the polyol; and b) reacting the product from step a) with glycidyl (meth)acrylate or allyl glycidyl ether in an amount of at least corresponding to 1 mol of glycidyl (meth)acrylate or allyl glycidyl ether per free carboxylic acid group of the product a); and c) product from the second step b) is further reacted with an unsaturated, aromatic or aliphatic anhydride in an amount sufficient to esterify a part of or all free hydroxyl groups of the product from step b).

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Hyperbranched polyesters

The present invention relates to hyperbranched polyesters, to a process for the manufacture thereof, to their use in unsaturated polyester preparations and to curable resins comprising hyperbranched polyesters.

The conventional curable polyester resins generally comprise oligomers and comonomers, and oligomers usually consist of linear molecular chains. The viscosity of the resin increases significantly with increasing chain length of the oligomer. Thus, large amounts of multidimensional comonomers are required for viscosity control of formulas especially for applications, such as spraying, dipping and roll coating. Traditionally used comonomers affect the curing reaction and the properties of the final product. Comonomers often have low curing rate, they cause shrinkage of the film during curing, have high costs, limited shelf life and also many of them are volatile and toxic. The legislation in several countries covering environmental protection and occupational safety has tightened during the recent years and set limitations on emissions of volatile organic compounds (VOC), such as styrene, which is a commonly used comonomer in unsaturated polyester resins. Styrene content ranges from 35 % to 50 % in conventional resins. Several methods have been evaluated in order to reduce the amount of styrene in unsaturated polyester resins, and low styrene emission (LSE) resins have been developed with styrene contents below 35 %. LSE resins may contain additives which lower the emissions, or they are suppressed resins, new monomer resins, resins with reduced styrene contents, high solids resins or resins where styrene is totally or partly replaced with another monomer. The most commonly used method to reduce styrene emissions is to use film forming additives, such as paraffin in the resins.

Oligomers with a highly branched structure and with a spherical shape constitute a family of polymers, which has been increasingly studied during recent years. These oligomers are referred to as hyperbranched polyesters having three-dimensional

molecular architecture and possessing starburst topology. These polymers are also named as dendritic polymers or dendrimers. Hyperbranched polyesters differ significantly from conventional linear oligomers, because the linear oligomer of sufficient molecular weight for polyester resins usually contains an entanglement of flexible molecular chains, usually only with two terminal functional groups on each molecule, while the hyperbranched polyester is a compact spherical molecule with many branches which carry a high number of terminal functional groups on each molecule. These unique features of the hyperbranched polyesters yield interesting and special properties which make these compounds very attractive and useful in several applications. The spherical shape yields the compounds favourable and different rheological properties, such as lower viscosity, when compared with the conventional linear oligomers. The high number of terminal, functional groups, which can be modified, results in a variety of physical and chemical properties. Oligomers with a strongly branched structure can be used in applications, such as catalysts, as carriers for drug substances in pharmaceutical industry, as pharmaceuticals, cosmetics, adhesives, coatings, composites, agricultural chemicals and as multifunctional crosslinking agents.

A series of hyperbranched (meth)acrylated polyesters with different number of terminal double bonds per molecule has been presented and methods for the manufacture thereof have been disclosed in the patent application WO 96/07688. This publication discloses a hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride, and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups. Further, in the hyperbranched polyester, (meth)acrylic anhydride and/or an aliphatic carboxylic anhydride form ester linkages with free hydroxyl groups. The said hyperbranched polyesters can be used as resins which are curable by UV-radiation. The method for the manufacture of said hyperbranched polyesters comprises reacting an aromatic polycarboxylic anhydride with a polyol with 3 to 10 reactive hydroxyl groups in the presence of an activating agent

stannous chloride and reacting the obtained product with glycidyl (meth)acrylate or allyl glycidyl ether.

An object of the present invention is to provide an improved, economical and on an industrial scale applicable process for the manufacture of hyperbranched polyesters.

A further object of the invention is to present new hyperbranched polyesters.

A further object of the invention is to provide hyperbranched polyesters which in unsaturated polyester applications require low amounts of mono- or multifunctional comonomer while the resins still retain a low viscosity, a high curing rate, an acceptable degree of curing and the final products manufactured thereof exhibit good mechanical properties, and the curing can be performed applying any suitable curing methods.

The objects of the invention are achieved by a method for the manufacture of hyperbranched polyesters, by new hyperbranched polyesters and by resins comprising them, as claimed in the claims.

Characteristics of the method, the polyesters, the resins and the use are stated in the claims.

It has been found that according to the invention new hyperbranched polyesters can be manufactured and an improved method for the manufacture of the hyperbranched polyesters can be provided. Thus, the present invention relates to hyperbranched polyesters of a polyol with 2 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, and a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably with 3 carboxyl groups, each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride, and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkage with the remaining carboxyl groups of the anhydride and free hydroxyl groups, and further unsaturated, aromatic or aliphatic anhydride forming ester linkages with free hydroxyl

groups. The present invention further relates to a process for the manufacture of said hyperbranched polyester.

The process is a controlled stepwise divergent method with at least two reaction steps and the synthesis starts at the center of the hyperbranched polyester.

The process comprises the following steps:

First step

a) reacting a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably free carboxyl groups, with a polyol with 2 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, in the presence of an amine, the amount of anhydride being at least 1 mol of anhydride per hydroxyl group of the polyol,

Second step

b) reacting the product from step a) with glycidyl (meth)acrylate or allyl glycidyl ether in an amount of at least corresponding to 1 mol of glycidyl (meth)acrylate or allyl glycidyl ether per free carboxylic acid group of the product of a),

Third step

c) the product from the second step b) is further reacted with an unsaturated, aromatic or aliphatic anhydride in an amount sufficient to esterify a part or all free hydroxyl groups of the product from step b).

In the first reaction step, a polycarboxylic anhydride with 2 to 4 carboxyl groups is heated to a temperature of about or below 100 °C, preferably below 80 °C in the presence of a solvent or a mixture of solvents, in the presence of a tertiary aliphatic or aromatic amine, preferably triethylamine as a catalyst and under inert gas atmosphere, preferably under nitrogen atmosphere. The polycarboxylic anhydride is

preferably an aromatic anhydride. such as trimellitic anhydride or phthalic anhydride. Suitable polyols are polyols having 2 to 10 hydroxyl groups and the hydroxyl groups are preferably of equivalent reactivity, which allows the esterification of each of the hydroxyl groups to proceed equally easily in order to start the building up of the regular molecule. Examples of suitable polyols are pentaeryhtritol, dipentaerythritol, trimethyloyl propane, neopentyl glycol and the like. The amount of added anhydride is at least one mol of anhydride per hydroxyl group of the polyol but preferably the anhydride is added in an excess amount. An excess of 5—50 mol% is suitable. A suitable solvent is dimethylformamide or 1-methyl-2-pyrrolidinone or a mixture thereof. The reaction mixture can be used as such without further purification for the following step of the process.

In the second step, the intermediate from the first reaction step is allowed to react with glycidyl (meth)acrylate or allyl glycidyl ether in an amount at least corresponding to one mol of glycidyl (meth)acrylate or allyl glycidyl ether per free carboxylic acid group of the formed polyester, preferably in an excess amount of about 5—20 wt%. Preferred reactant is glycidyl (meth)acrylate. The reaction is carried out in a solvent, such as dimethyl formamide or 1-methyl-2-pyrrolidinone or a mixture thereof, in the presence of an inhibitor for radical polymerization. A suitable inhibitor is hydroquinone monomethyl ether. The amine from the previous reaction step, preferably triethylamine acts as a basic catalyst. The reaction temperature is below 100 °C, preferably below 80 °C. The obtained second intermediate reaction mixture can be used without further purification in the following reaction step.

In the third reaction step, the hydroxyl groups of the hyperbranched polyester with terminal double bonds are reacted further by ester formation with an unsaturated, aromatic or aliphatic anhydride, preferably acetic anhydride or (meth)acrylic anhydride, in an amount sufficient to esterify part or all of the free hydroxyl groups in order to prepare the hyperbranched polyester molecules with acetyl groups or further end double bonds. The reaction is preferably performed at a temperature below 100 °C, preferably below 80 °C, in the presence of a solvent, such as

dimethyl formamide or 1-methyl-2-pyrrolidinone or a mixture thereof. Conveniently the solvents used in the previous reaction steps and remaining in the reaction mixture may act as solvents without additional solvents. After the reaction is completed, an inhibitor, preferably benzoquinone is added and the product may optionally be dissolved in an organic solvent which is immiscible with water, such as an aromatic hydrocarbon or a chlorinated hydrocarbon or a mixture thereof, suitably toluene or methylene chloride, for further processing. The product may also be dissolved in styrene in order to obtain a 40—70 % solution of the product in styrene. Styrene is especially favourable as the obtained solution can readily be used in unsaturated polyester resins without removal of the solvent. Other suitable solvents for the same purpose are p-methylstyrene or vinyltoluene. This solution can readily be used for the manufacture of resins and other applications.

Alternatively the third step c) may be omitted if hydroxy functional hyperbranched polyesters are desired. After the reaction is completed in step b), the product may optionally be dissolved in an organic solvent as described above in step c).

The process according to the invention is specially suitable for industrial scale without the drawbacks of the small scale methods according to prior art. New amine catalysts can be used in the process instead of stannous chloride, no isolation of intermediates is required in the process and no distillation of the solvents is needed.

The hyperbranched polyesters obtained with polyols containing two reactive hydroxyl groups, such as neopentyl glycol are new compounds with properties especially suitable to serve as reactive blendable comonomers in resins because of their favourable rheological properties.

The hyperbranched polyesters according to the invention, based on a polyol core molecule, a polycarboxylic anhydride as a branching extender and an epoxyacrylate as an end group can be used to improve the mechanical properties of high solids unsaturated resins with low conomomer contents while still retaining good mechanical properties of the resin. Thus, styrene contents of 30 % by weight or less can be used

which is clearly an advantage from an environmental point of view as the styrene emissions will be reduced. The hyperbranched polyesters can also be used in styrene free unsaturated polyester resins, which are based on vinyl ether monomers. The heat distortion temperature, tensile and flexural strength of cured polyester resins manufactured using hyperbranched polyesters according to the invention are improved when up to 15 % of the hyperbranched polyester or a mixture thereof is added into the high solids unsaturated polyester. The mechanical properties of the polyester resins thus obtained can be widely modified and adjusted according to the final use of the resin. The hyperbranched polyesters according to the invention can be used as resins which can be cured by conventional curing systems, such as thermally initiated curing using initiators, such as aliphatic azo compounds or organic peroxides, such as benzoyl peroxide, by a redox reaction initiated curing using organic peroxides, such as methyl ethyl ketone peroxide and metal salts, by photochemically initiated curing using UV-light or by radiation inititated curing by EB-radiation.

The resins have a lower viscosity than conventional oligomer resins and they can be used with or without comonomers. The resins may also comprise monofunctional or multifunctional comonomers or mixtures thereof, and a suitable amount of co-monomer is 5—20 wt%. As multifunctional comonomers, compounds with reactive double bonds, preferably with 1—6 (meth)acrylate or acrylate groups can be used, and such as trimethyloyl propane tri(meth)acrylate, hexanediol diacrylate, trimethyloyl propane triallyl ether, pentaerythritol tri/tetraallylether, triallyl cyanurate, trimethyloyl propane triacrylether and pentaerythritol tetraacrylether are suitable. As monofunctional comonomers vinyl aromatic monomers, such as styrene, p-methylstyrene or vinyl toluene are suitable. Also alkyl (meth)acrylates, such as methyl (meth)acrylate may be used. The resins according to the invention can be used in many different fields, such as coating, adhesives, laminates, foils, thin-films and composites.

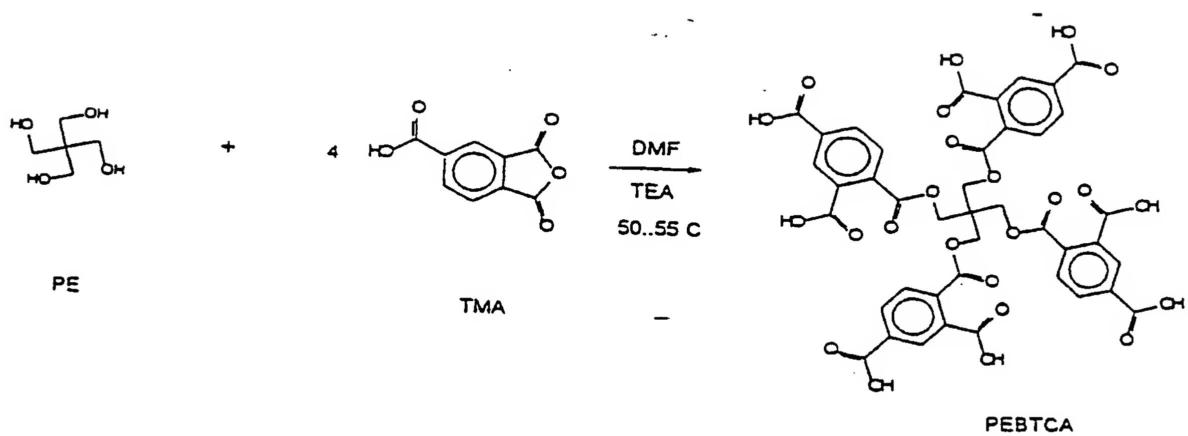
The following examples illustrate the invention in more detail however they are not intended to be limiting the invention.

Preparation and results of analysis of hyperbranched methacrylated polyesters

Example 1

1. Synthesis procedure of D1

Step 1. Synthesis of intermediate I PEBTCA



40.0 g (0.294 mol) of pentaerythritol (PE) and 40 ml of triethylamine (TEA) are dissolved in 400 ml of dimethylformamide (DMF). Then 248.0 g (1.29 mol, 10 % excess) of trimellitic anhydride (TMA) is added in portions within 30 min at a temperature below 55 °C. After the addition the reaction mixture is stirred at 50...55 °C under nitrogen atmosphere for 6 hours and cooled down to room temperature overnight.

The reaction mixture containing the intermediate I PEBTCA is analyzed by HPLC, ^{1}HNMR and acid number titration (TAN).

Typical analysis

Composition by high pressure liquid chromatography (HPLC):

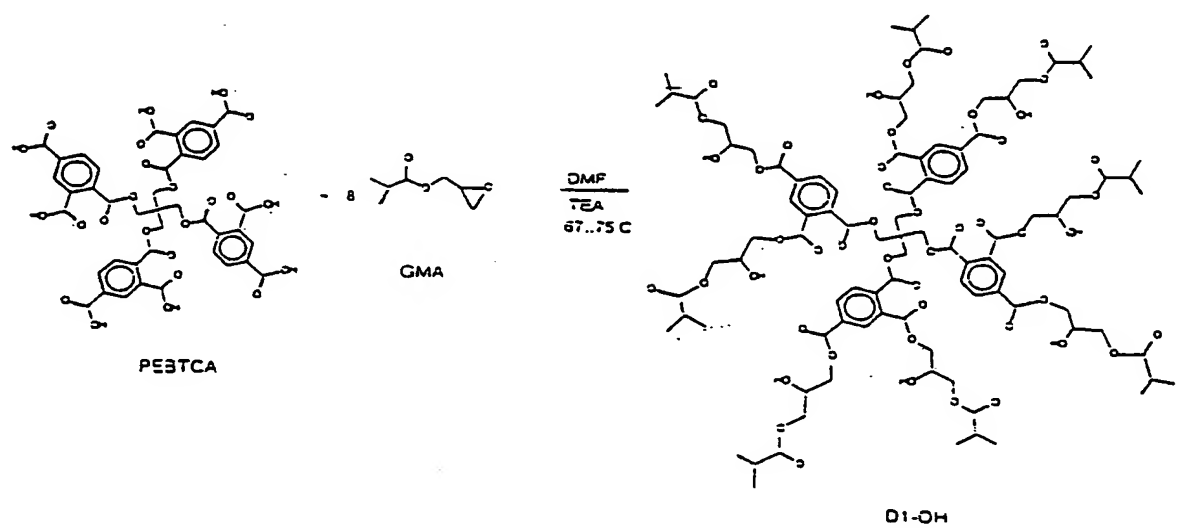
Tetraester	85...87 %
Triester	1.3 %
TMA + acid	10...11 %

Titrated acid number (TAN):

213...220 mg KOH/g (217 theoretical)

The reaction mixture is used in the next process step without further purification.

Step 2. Synthesis of intermediate II D1-OH



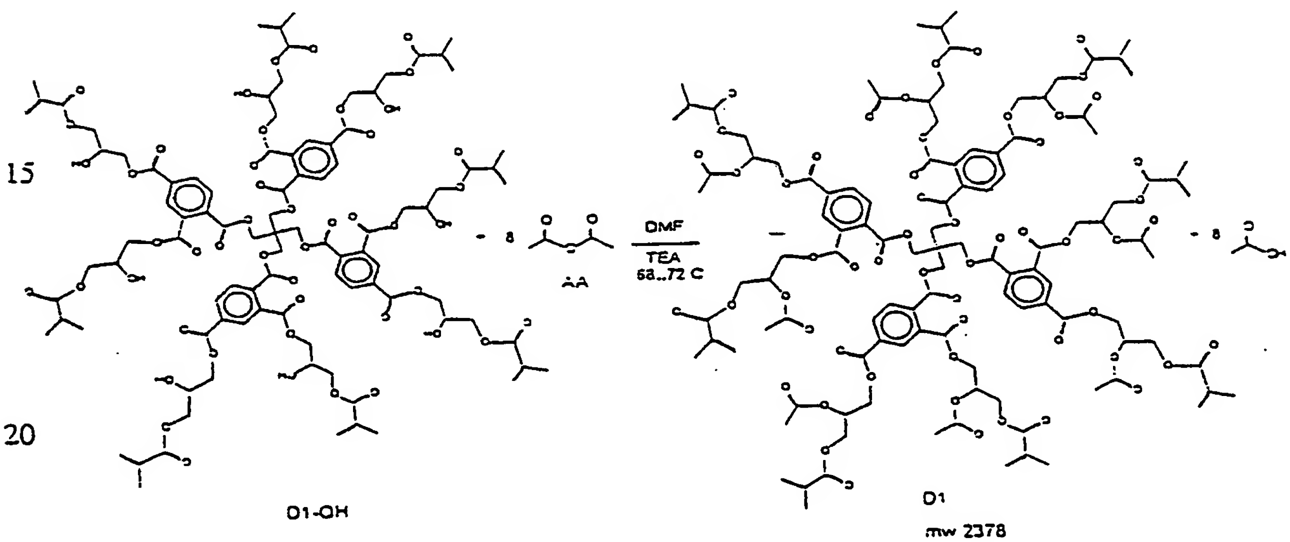
2.0 g of hydroquinone monomethyl ether (inhibitor) is added into the PEBTCA-reaction mixture from step 1 and the mixture is warmed up to 50...55 °C. Then 400.0 ml (2.94 mol, 10 % excess) of glycidyl methacrylate (GMA) is slowly added during 1...2 hours at a temperature below 75 °C. The reaction mixture is further

stirred at 70...75 °C for about 10 hours until TAN of the mixture is < 10 mg KOH/g.

The reaction mixture containing the intermediate D1-OH is analyzed by GPC, [1]HNMR and acid number titration (TAN).

The reaction mixture is used in the next step without further purification.

Step 3a. Synthesis of final product D1 (60 % solution in styrene)



350.0 g of the reaction mixture containing the intermediare D1-OH from step 2 is warmed up to 50...55 °C. 75.0 ml (0.80 mol) of acetic anhydride (AA) is slowly added during 20 min at 50...70 °C. After the addition the mixture is stirred at 68...72 °C for 3 hours. Then 550 ml of styrene is added to dissolve the product and the solution is washed with 700 ml of 10 % Na_2CO_3 at 55...60 °C. After separation of the layers another 150 ml of styrene is added and the mixture is washed with 700 ml of water at 55...60 °C. Then 0.25 g of benzoquinone is added and the product

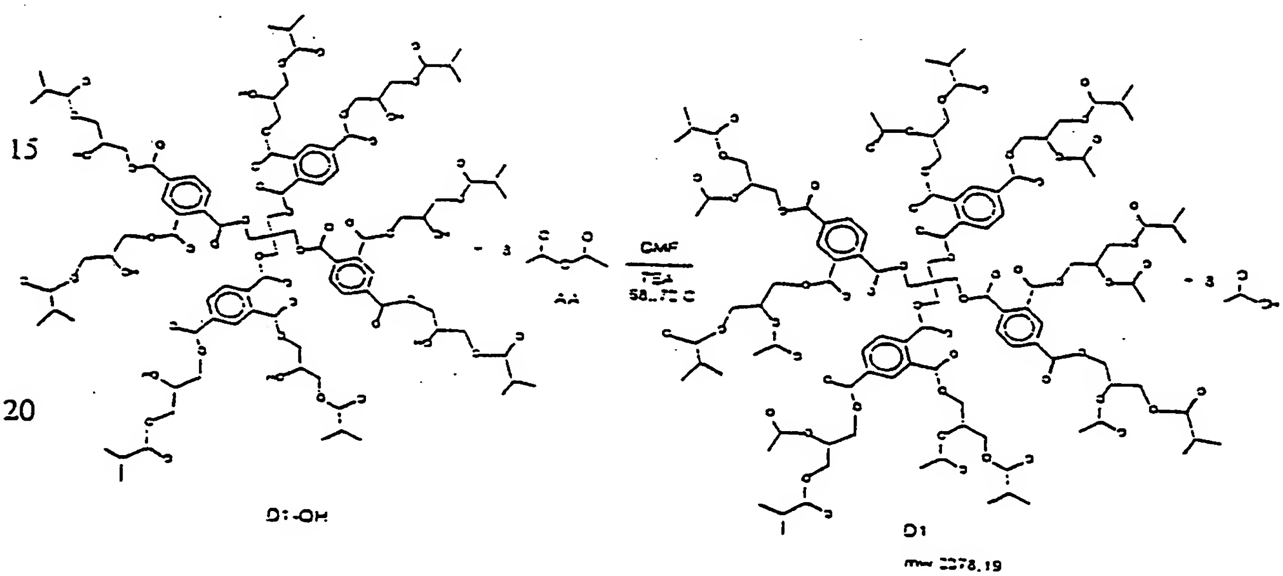
is distilled under vacuum below 70 °C / 50 mbar in order to remove residual water (about 13 ml) and a part of styrene (about 550 ml) from the mixture.

Yield is 380 g of about 60 % D1-solution in styrene.

The structure of the product is confirmed by [1]HNMR and GPC.

Alternatively D1 can be obtained as a viscous oil according to the following procedure Step 3b.

Step 3b. Synthesis of D1



350.0 g of the reaction mixture containing the intermediate D1-OH from step 2 is warmed up to 50...55 °C. 75.0 ml (0.80 mol) acetic anhydride (AA) is slowly added during 20 min at 50...70 °C. After the addition, the mixture is stirred at 68...72 °C for 3 hours. Then, 550 ml of toluene is added to dissolve the product and the

solution is washed with 700 ml of 10 % Na_2CO_3 at 55...60 °C. After separation of the layers another 150 ml of toluene is added and the mixture is washed with 700 ml of water at 55...60 °C. Then 0.25 g of benzoquinone is added and the product is distilled under vacuum below 70 °C / 30 mbar in order to remove residual water (about 10 ml) and toluene (about 700 ml) from the mixture.

Yield is 250 g of D1 (highly viscous oil).

The structure of the product is confirmed by ^{1}HNMR and GPC.

Preparation of hyperbranched methacrylated polyesters starting from polyols

Example 2

Intermediates II: PGL-OH, DPGL-OH, DD1-OH, TMPA-OH, DTMP-OH and NGL-OH are synthetisized and analyzed in the same way as D1-OH described in Example 1. No intermediate I is isolated and Steps 1 and 2 are combined. Table 1 summarizes average amounts of starting materials used in the synthesis of intermediates II.

Table 1

Starting materials	Intermediate II					
	PGL-OH	DPGL-OH	DD1-OH	TMPA-OH	DTMP-OH	NGL-OH
Dimethylformamide	300 ml	400 ml	400 ml	400 ml	380 ml	400 ml
Pentaerythritol	60 g					
Dipentaerythritol		80 g	50 g			
Trimethyloylpropane				80 g	50 g	
Neopentyl glycol						60 g
Triethylamine	30 ml	35 ml	40 ml	30 ml	37 ml	35 ml
Trimellitic anhydride			240 g		235 g	235 g
Phthalic anhydride	280 g	300 g		280 g		
HQ-monomethylether	2 g	2 g	2 g	2 g	1.7 g	2 g
Glycidyl methacrylate	300 ml	320 ml	385 ml	300 ml	380 ml	375 ml

Final products PGL, PMA, DPGL, DPMA, DD1, DD3, TMPA, TMPM, DTMP, NGL and NMA are synthetisized and analyzed in the same way as D1 described in Example 1, Step 3. Table 2 summarizes the average amounts of starting materials used in the synthesis of the earlier mentioned final products.

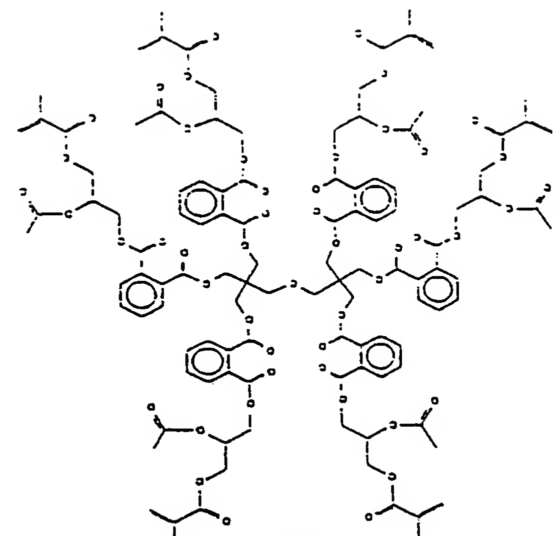
The chemical structures of obtained hyperbranched polyesters D1 (mw 2378), DTMP (mw 1815), PGL (mw 1465), PMA (mw 1569), DPGL (mw 2248), DPMA (mw 2404), DD3 (mw 3929), DD1 (mw 3617), NMA (mw 1329), NGL (mw 1225), TMPM (mw 1209) and TMPA (mw 1131) are presented in the following.

All the processes described above, can easily be scaled up to larger industrial scales with commercial batch sizes.

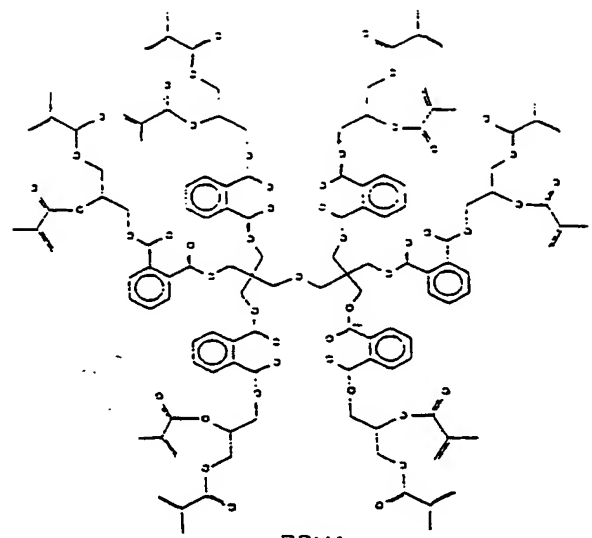
Table 2

Starting material	Final product										
	PGL	PMA	DPGL	DPMA	DD1	DD3	TMPA	TMPM	DTMP	NGL	NMA
PGL-OH reaction mixture	250 g	250 g									
DPGL-OH reaction mixture			250 g	250 g							
DD1-OH reaction mixture					250 g	350 g					
TMPA-OH reaction mixture							250 g	350 g			
DTMP-OH reaction mixture									200 g		
NGL-OH reaction mixture										250 g	350 g
Acetanhydride	44 ml		44 ml		55 ml		43 ml		43 ml	54 ml	
Methacrylic anhydride		70 ml		70 ml		122 ml		95 ml			120 ml
Benzoquinone	0.1 g	0.1 g	0.1 g	0.1 g	0.1 g	0.2 g	0.1 g	0.15 g	0.1 g	0.1 g	0.2 g
Toluene	500 ml	500 ml	500 ml	500 ml	500 ml		500 ml		400 ml	500 ml	
Styrene						700 ml		700 ml			700 ml
10% Na-carbonate	500 ml	500 ml	500 ml	500 ml	500 ml	700 ml	500 ml	700 ml	400 ml	500 ml	700 ml
Yield	169 g	188 g	174 g	189 g	177 g	420 g[1]	170 g	415 g[1]	142 g	176 g	440 g[1]

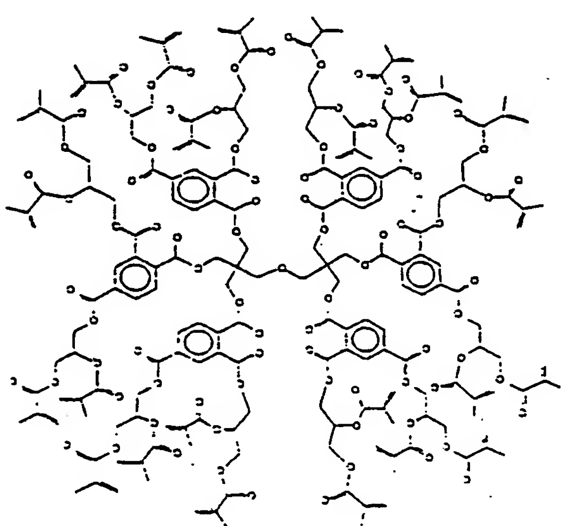
[1] 60 % solution in styrene



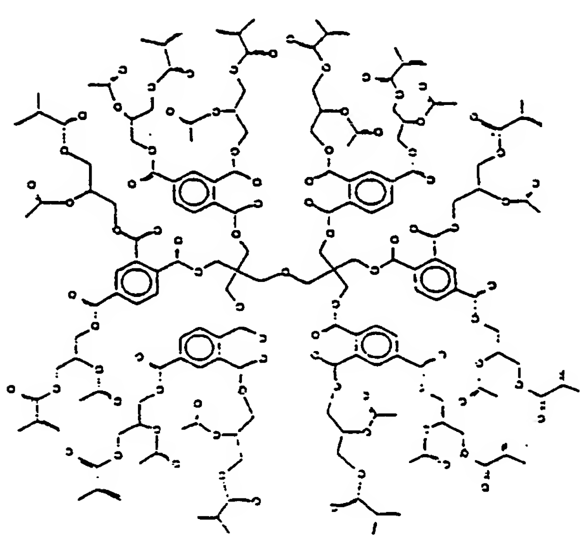
DPGL



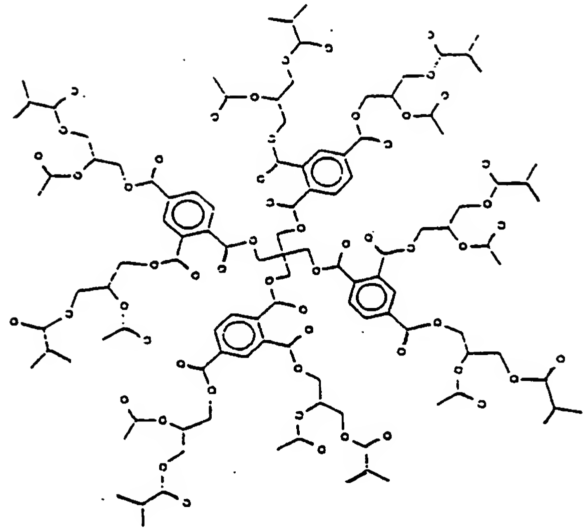
DPMA



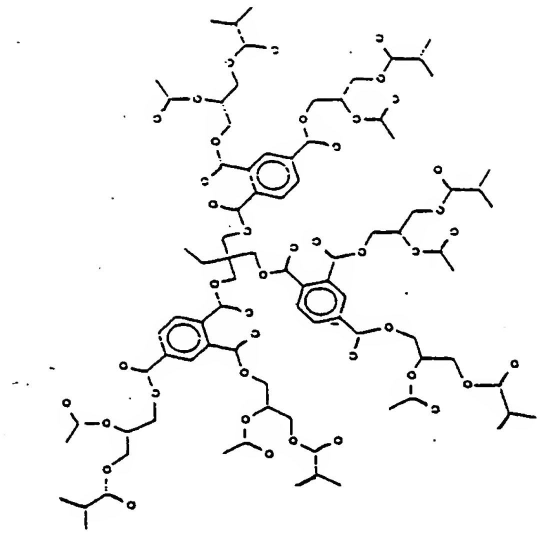
DD3



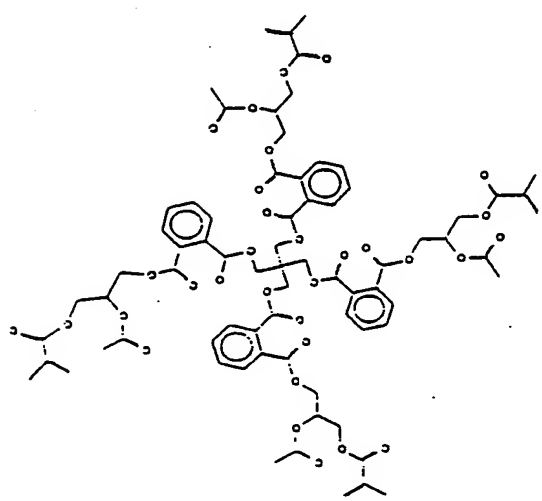
DD1



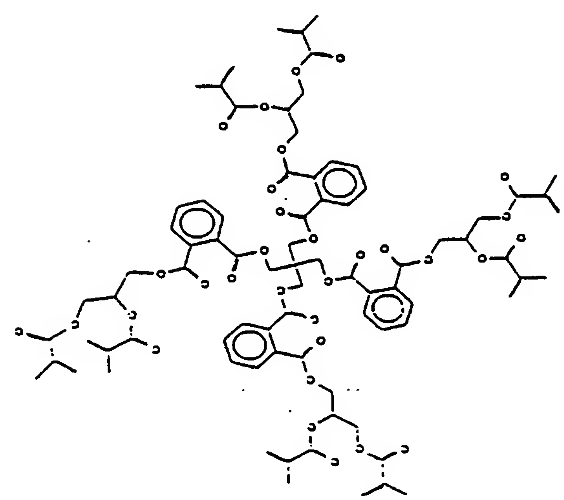
D1



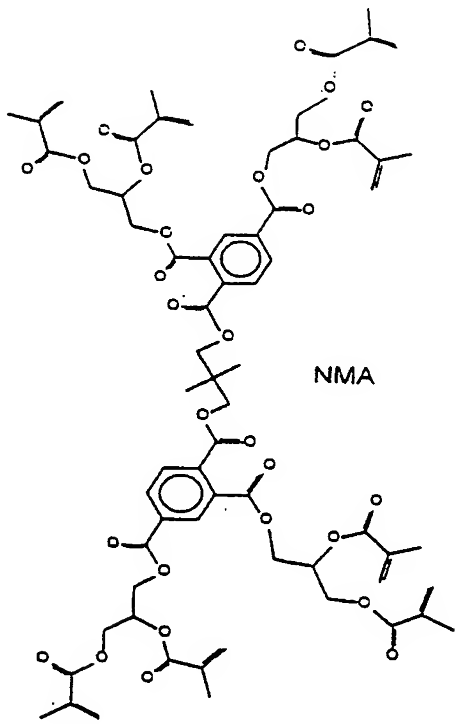
DTMP



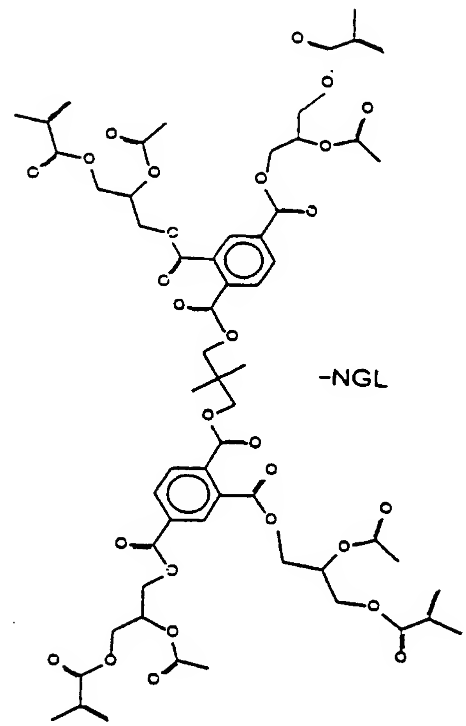
PGL



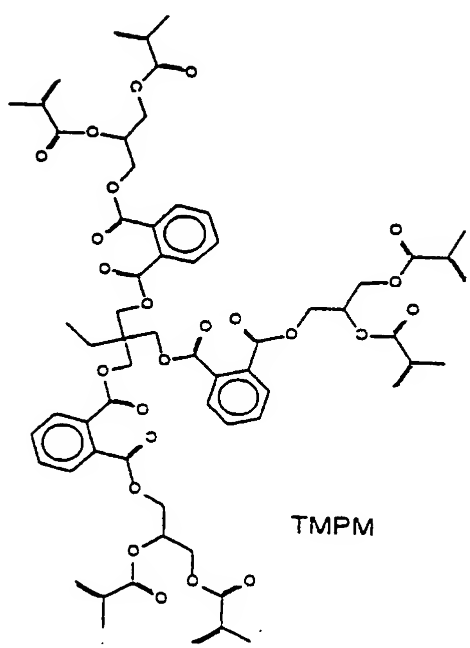
PMA



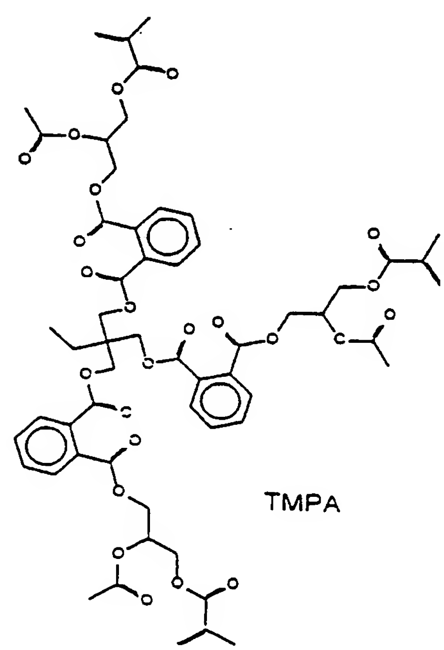
NMA



-NGL



TMPM



TMPA

Example 3

Testing of mechanical properties

The mechanical properties of blends of hyperbranched polyesters and unsaturated polyesters are tested from castings prepared as follows:

Resin mixture preparation

Resin blends are prepared by mixing the unsaturated polyester resin with various amounts of hyperbranched polyesters. The styrene content is 30 % in all blends. The unsaturated polyester is a low molecular weight polyester made from orthophthalic anhydride, maleic anhydride and 1,2-propanediol. The amount of hyperbranched polyesters is 5 wt%, 10 wt-% and 15 wt%. The resin blend is cured with 0.4 wt% of promoter (a mixture of cobalt octoate, dimethyl aniline and methyl hydroquinone) and 1 wt% methyl ethyl ketone peroxide. As a reference, a commercial monomer trimethyloylpropane trimethacrylate is blended with the same polyester in the same way.

Preparation of castings

The casting is prepared at room temperature using a metal frame. The surface of the frame is Teflon treated in order to prevent sticking of the resin to the metal. The outer size of the frame is 25.5 x 40.5 cm, the inner size is 26 x 21 cm. The thickness of the frame is 4 mm.

The frame is placed on a glass plate covered with Melinex (PET) foil. 400 g of resin is weighed, and air is removed with vacuum. The needed amount of peroxide is then added, and the resin is mixed without causing air-bubble formation.

The resin is poured carefully into the mold, and the mold is then covered with a Melinex film, and a glass plate. A metal plate is put on top as a weight.

The casting is left to cure overnight at room temperature.

The casting is then checked for residual stresses between two Polaroid plastic films, on a light table.

Mechanical testing

Specimens for mechanical testing are cut using a machine saw.

After cutting the specimens are post-cured at 50 °C for 24 hours. The specimens are placed between two glass plates in an oven. The specimens are cooled slowly to room temperature (1 h) to decrease residual stresses. The tested samples are then checked between two Polaroid films for residual stresses, and the specimens with least residual stresses are selected. At least five specimens are selected.

The mechanical test is made using an Instron 1175, with a 5 kN load cell. The crosshead speed is 2 mm/min.

Heat distortion temperature

The heat distortion temperature (HDT = temperature of deflection under load) is measured from specimens cut from the castings, size 10 mm x 110 mm.

The specimens are post-cured and checked in the same way as the specimens for the mechanical testing.

The HDT value is measured in a heating bath, which is heated from 20 °C at a rate of 2 C°/min. The specimen is loaded using a constant load. The temperature at which the specimen bends is registered as the HDT value.

Results of cured resins containing hyperbranched polyesters are provided in the following Tables 3—15.

Table 3

Resin with D1

	A	B	C	D
Amount of D1 (wt%)	0	5	10	15
Tensile strength (MPa)	43	48	50	53
Tensile modulus (MPa)	2393	2635	2729	2778
Tensile elongation (%)	5.3	3.7	3.7	3.7
Heat distortion temperature HDT (°C)	53	58	64	64

Table 4

Resin with PGL

	A	B	C	D
Amount of PGL (wt%)	0	5	10	15
Tensile strength (MPa)	52	55	61	59
Tensile modulus (MPa)	2791	2911	3000	3152
Tensile elongation (%)	2.7	2.8	3.5	2.9
Bending (mm)	7.8	9.3	10.2	8.1
Bending strength (MPa)	112	114	119	122
Bending modulus (MPa)	2684	2680	2690	2929
Heat distorion temperature HDT (°C)	62	63	65	64

Table 5

Resin with PMA

	A	B	C	D
Amount of PMA (wt%)	0	5	10	15
Tensile strength (MPa)	52	50	54	46
Tensile modulus (MPa)	2917	2931	3108	3161
Tensile elongation (%)	2.6	2.2	2.2	1.7
Bending (mm)	8.3	8.6	6.3	7.9
Bending strength (MPa)	105	107	100	118
Bending modulus (MPa)	2645	2660	2850	2978
Heat distortion temperature HDT (°C)	63	66	69	72

Table 6

Resin with DPGL

	A	B	C	D
Amount of DPGL (wt%)	0	5	10	15
Tensile strength (MPa)	52	55	60	54
Tensile modulus (MPa)	2917	2964	3334	3226
Tensile elongation (%)	2.6	2.5	2.8	2.2
Bending (mm)	8.3	8.1	9.2	8.4
Bending strength (MPa)	105	112	116	116
Bending modulus (MPa)	2645	2886	2886	2898
Heat distortion temperature HDT (°C)	63	66	70	69

Table 7

Resin with DPMA

	A	B	C
Amount of DPMA (wt%)	0	5	10
Tensile strength (MPa)	52	50	49
Tensile modulus (MPa)	2917	2952	3058
Tensile elongation (%)	2.6	2.3	2
Bending (mm)	8.3	7.2	8.1
Bending strength (MPa)	105	108	115
Bending modulus (MPa)	2645	2783	2852
Heat distortion temperature HDT (°C)	65	65	69

Table 8

Resin with DD1

	A	B	C
Amount of DD1 (wt%)	0	5	10
Tensile strength (MPa)	46	46	43
Tensile modulus (MPa)	2560	2604	2588
Tensile elongation (%)	2.9	2.7	2
Bending strength (MPa)	82	86	82
Bending modulus (MPa)	2175	2338	2336
Heat distortion temperature HDT (°C)	63	64	67

Table 9

Resin with DD3

	A	B	C	D
Amount of DD3 (wt%)	0	5	10	15
Tensile strength (MPa)	46	46	34	28
Tensile modulus (MPa)	2560	2726	2846	2995
Tensile elongation (%)	2.9	2.2	1.3	1
Bending strength (MPa)	82	78	79	88
Bending modulus (MPa)	2175	2259	2292	2433
Heat distortion temperature HDT (°C)	63	65	67	68

Table 10

Resin with TMPA

	A	B	C
Amount of TMPA (wt%)	0	5	10
Tensile strength (MPa)	46	49	50
Tensile modulus (MPa)	2560	2578	2690
Tensile elongation (%)	2.9	3.2	3.1
Bending strength (MPa)	82	88	88
Bending modulus (MPa)	2175	2401	2410
Heat distortion temperature HDT (°C)	63	64	64

Table 11

Resin with TMPM

	A	B	C	D
Amount of TMPM (wt%)	0	5	10	15
Tensile strength (MPa)	46	46	47	46
Tensile modulus (MPa)	2560	2657	2801	2880
Tensile elongation (%)	2.9	2.6	2.2	2.1
Bending strength (MPa)	82	86	95	95
Bending modulus (MPa)	2175	2356	2509	2562
Heat distortion temperature HDT (°C)	63	65	67	69

Table 12

Resin with DTMP

	A	B	C
Amount of DTMP (wt%)	0	5	10
Tensile strength (MPa)	50	53	52
Tensile modulus (MPa)	2501	2667	2546
Tensile elongation (%)	3.9	3.8	3.4
Bending (mm)	9.4	10.3	10
Bending strength (MPa)	90	98	100
Bending modulus (MPa)	2233	2340	2412
Heat distortion temperature HDT (°C)	58	59	63

Table 13

Resin with NGL

	A	B	C
Amount of NGL (wt%)	0	5	10
Tensile strength (MPa)	53	55	51
Tensile modulus (MPa)	2899	3025	2783
Tensile elongation (%)	3.1	3	2.8
Bending strength (MPa)	89	70	85
Bending modulus (MPa)	2428	1726	2245
Heat distortion temperature HDT (°C)	61	64	64

Table 14

Resin with NMA

	A	B	C
Amount of NMA (wt%)	0	5	10
Tensile strength (MPa)	53	53	46
Tensile modulus (MPa)	2899	2957	2803
Tensile elongation (%)	3.1	2.6	2.1
Bending strength (MPa)	89	87	91
Bending modulus (MPa)	2428	1915	2527
Heat distortion temperature HDT (°C)	61	62	65

Table 15

Reference resin containing trimethyloylpropane trimethacrylate (TMPTMA)

	A	B	C	D
Amount of TMPTMA (wt%)	0	5	10	15
Tensile strength (MPa)	50	46	34	32
Tensile modulus (MPa)	2830	2967	2961	3045
Tensile elongation (%)	2.4	2	1.3	1.2
Bending (mm)	8.4	7.8	6.8	6.6
Bending strength (MPa)	102	110	103	104
Bending modulus (MPa)	2520	2755	2858	2870
Heat distortion temperature HDT (°C)	63	66	67	70

Claims

1. A process for the manufacture of hyperbranched polyesters, **characterized** in that the process comprises the following steps:

a) reacting a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably free carboxyl groups, with a polyol with 2 to10 reactive hydroxyl groups, preferably of equivalent reactivity, in the presence of an amine, the amount of anhydride being at least 1 mol of anhydride per hydroxyl group of the polyol, and

b) reacting the product from step a) with glycidyl (meth)acrylate or allyl glycidyl ether in an amount of at least corresponding to 1 mol of glycidyl (meth)acrylate or allyl glycidyl ether per free carboxylic acid group of the product a), and

c) product from the second step b) is further reacted with an unsaturated, aromatic or aliphatic anhydride in an amount sufficient to esterify a part of or all free hydroxyl groups of the product from step b).

2. A process according to claim 1, **characterized** in that the amine is a tertiary aliphatic or aromatic amine, preferably triethylamine.

3. A process according to claim 1 or 2, **characterized** in that the reaction is carried out in the step a) at a temperature below 100 °C, preferably below 80 °C in the presence of an organic solvent or mixture of solvents, the second step b) at a temperature below 100 °C, preferably below 80 °C in the presence of an organic solvent or mixture of solvents, and the third step c) at a temperature below 100 °C, preferably below 80 °C in the presence of an organic solvent or mixture of solvents.

4. A process according to any one of claims 1—3, **characterized** in that the amount of anhydride in step a) and of acrylate in step b) are in excess of the stated amount.

5. A process according to any one of claims 1—4, **characterized** in that the reaction of step b) is performed in the presence of a basic catalyst and an inhibitor for radical polymerization and in step c) an inhibitor is used.

6. A process according to claim 5, **characterized** in that the basic catalyst is the amine used in step a).

7. A process according to claim 5 or 6, **characterized** in that the inhibitor in step b) is hydroquinone monomethyl ether and in step c) the inhibitor is benzoquinone.

8. A process according to any one of claims 1—7, **characterized** in that polycarboxylic anhydride is trimellitic anhydride or phthalic anhydride.

9. A process according to any one of claims 1—8, **characterized** in that the polyol is pentaerythritol, dipentaerythritol, trimethyloylpropane or neopentyl glycol.

10. A process according to any one of claims 1—9, **characterized** in that the anhydride in step c) is (meth)acrylic anhydride or acetic anhydride.

11. A process according to any one of claims 1—10, **characterized** in that the product from step a) is allowed to react with glycidyl methacrylate.

12. A process according to any one of claims 1—11, **characterized** in that the solvent used in step a) is dimethylformamide or 1-methyl-2-pyrrolidinone, in step b) dimethylformamide or 1-methyl-2-pyrrolidinone and in step c) dimethylformamide or 1-methyl-2-pyrrolidinone, and after the reaction in step c) the product may optionally be dissolved in an aromatic hydrocarbon or a chlorinated hydrocarbon, preferably styrene, p-methylstyrene, vinyltoluene, toluene or methylene chloride.

13. A hyperbranched polyester of a polyol comprising two reactive hydroxyl groups, preferably of equivalent reactivity, and a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups, each hydroxyl group of the polyol

forming an ester-linkage with one anhydride group of the polycarboxylic anhydride and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester-linkages with the remaning carboxyl groups of the anhydride and free hydroxyl groups, and further unsaturated aromatic or aliphatic anhydride forming ester-linkages with free hydroxyl groups.

14. A process for the manufacture of hyperbranched polyesters, **characterized** in that the process comprises the following steps:

a) reacting a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably free carboxyl groups, with a polyol with 2 to 10 reactive hydroxyl groups, preferably of equivalent reactivity, in the presence of an amine, the amount of anhydride being at least 1 mol of anhydride per hydroxyl froup of the polyol, and

b) reacting the product from step a) with glycidyl (meth)acrylate or allyl glycidyl ether in an amount of at least corresponding to 1 mol of glycidyl (meth)acrylate or allyl glycidyl ether per free carboxylic acid group of the product of a).

15. A process according to claim 14, **characterized** in that the amine is a tertiary aliphatic or aromatic amine, preferably triethylamine.

16. A process according to claim 14 or 15, **characterized** in that the reaction is carried out in the step a) at a temperature below 100 °C, preferably below 80 °C in the presence of an organic solvent or mixture of solvents, and in the second step b) at a temperature below 100 °C, preferably below 80 °C in the presence of an organic solvent or mixture of solvents.

17. A process according to any one of claims 14—16, **characterized** in that the amount of anhydride in step a) and of acrylate in step b) are in excess of stated amount.

18. A process according to any one of claims 14—17, **characterized** in that the reaction of step b) is performed in the presence of a basic catalyst and an inhibitor for radical polymerization.

19. A process according to claim 18, **characterized** in that the basic catalyst is the amine used in step a).

20. A process according to claim 18 or 19, **characterized** in that the inhibitor for radical polymerization is hydroquinone monomethyl ether.

21. A process according to any one of claims 14—20, **characterized** in that polycarboxylic anhydride is trimellitic anhydride or phthalic anhydride.

22. A process according to any one of claims 14—21, **characterized** in that the polyol is pentaerythritol, dipentaerythritol, trimethyloylpropane or neopentyl glycol.

23. A process according to any one of claims 14—22, **characterized** in that the product from step a) is allowed to react with glycidyl methacrylate.

24. A process according to any one of claims 14—23, **characterized** in that the solvent used in step a) is dimethylformamide or 1-methyl-2-pyrrolidinone, in step b) dimethylformamide or 1-methyl-2-pyrrolidinone, and after the reaction in step b) the product may optionally be dissolved in an aromatic hydrocarbon or a chlorinated hydrocarbon, preferably styrene, p-methylstyrene, vinyltoluene, toluene or methylene chloride.

25. A hyperbranched polyester of a polyol comprising two reactive hydroxyl groups, preferably of equivalent reactivity, and a polycarboxylic anhydride with 2 to 4 carboxyl groups, preferably 3 carboxyl groups, each hydroxyl group of the polyol forming an ester-linkage with one anhydride group of the polycarboxylic anhydride and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester-linkages with the remaining carboxyl groups of the anhydride and the free hydroxyl groups.

26. A curable resin, characterized in that it comprises at least one hyperbranched polyester defined in claim 13 or 25.

27. A curable resin, characterized in that it comprises at least one hyperbranched polyester obtainable by a process according to any one of claims 1—12 or 14—24.

28. A curable resin according to claim 26 or 27, characterized in that it further comprises a mono- or multifunctional comonomer, or a mixture thereof.

29. A curable resin according to any one of claims 26—28, characterized in that the comonomer comprises 1—6 methacrylate or acrylate groups, or it is a vinyl aromatic monomer or a mixture thereof.

30. A curable resin according to any one of claims 26—29, characterized in that the resin is cured by thermally initiated curing, by redox reaction initiated curing, by photochemically initiated curing or by radiation initiated curing.

31. Use of curable resin according to any one of claims 26—30 for the production of coatings, adhesives, laminates, foils, thin films and reinforced composites.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 00/00288

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08G 63/20, C08G 63/87
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	J. Am. Chem. Soc., Volume 118, 1996, Henrik Ihre et al, "Synthesis, Characterization, and 1H NMR Self-Diffusion Studies of Dendritic Aliphatic Polyesters Based on 2, 2-Bis(hydroxymethyl)propionic Acid and 1,1, 1-Tris(hydroxyphenyl)ethane", page 6388 - page 6395, page 6389, column 1, experimental section pages 6393-6395	1-12,27
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X	WO 9607688 A1 (INSTITUTET POLYMERUTVECKLING AB), 14 March 1996 (14.03.96), abstract; claims 1,27-29	13,26,28-31
Y	examples; claims; abstract	1-12,27
	--	

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2000	29 -08- 2000
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Ellen Setréus/Els Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 00/00288

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	STN International, file CAPLUS, CAPLUS accession no. 1972:420347, Document no. 77:20347, Mendeleev, D. I., Chemical-Technological Institute, Moscow: "Polyesters"; & SU,328124, 19720202 --	1-13
A	STN International, file CAPLUS, CAPLUS accession no. 1972:141757, Document no. 76:141757, Japan Oils and Fats Co., Ltd.: "Unsaturated polyesters"; & JP,B4,46041379, 19711207 --	1-13
A	Polymer, Volume 38, No 19, 1997, E. Malmström et al:, "Relaxation processes in hyperbranched polyesters: influence of terminal groups", page 4873 - page 4879, experimentals pages 4874-4875 --	1-13
A	Polymer Journal, Volume 26, No 2, 1994, K. L. Wooley et al, "One-Step Synthesis of Hyperbranched Polyesters. Molecular Weight Control and Chain End Functionalization", page 187 - page 197, table 1, page 189 - page 191, column 1 --	1-13
A	JP 11001550 A (MITSUI PETROCHEM IND CO LTD) 1999-01-06 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 2000-07-05). Retrieved from: EPO WPI Database. DW199911, Accession no. 1999-125518; & JP 11001550 A (MITSUI CHEM INC) 1999-04-30 (abstract). (online) (retrieved on 2000-07-05). Retrieved from: EPOPAJ Database --	1-13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 00/00288

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 9221543 A (KAO CORP) 1997-08-26 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 2000-07-05). Retrieved from: EPO WPI Database. DW199744, Accession No. 1997-475503; & JP 9221543 A (KAO CORP) 1997-12-25 (abstract). (online) (retrieved on 2000-07-05). Retrieved from: EPO PAJ Database --	1-13
A	Journal of dental research., Volume 70, No 1, 1991, M. Farahani et al, "The Effect of Catalyst Structure on the Synthesis of a Dental Restorative Monomer", page 67 - page 71, table --	1
A	FI 923817 A (NESTE OY), 27 February 1994 (27.02.94) -- --------	1-13

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).:

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see next page

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-13, 26-31

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Invention I: Claims 1-13 and 26-31 relate to a hyperbranched polyester, to a process for producing the said polyester and to the use of the said polyester in unsaturated polyester preparations and in curable resins. The hyperbranched polyester is characterised by its manufacturing process. The process is characterised in that is comprises 3 steps. In the first step a polyol is reacted with a polycarboxylic anhydride in the presence of an amine. In step two the product of the first step is reacted with glycidyl methacrylate or allyl glycidyl ether. In step three the product of the two is reacted with an unsaturated aromatic or aliphatic anhydride. The anhydride is in an amount sufficient to esterify a part or all free hydroxyl groups of the product of step two.

Invention II: Claims 14-31 relate to a hyperbranched polyester, to a process for producing the said polyester and to the use of the said polyester in unsaturated polyester preparations and in curable resins. The hyperbranched polyester is characterised by its manufacturing process. The process is characterised in that is comprises 2 steps. In the first step a polyol is reacted with a polycarboxylic anhydride in the presence of an amine. In step two the product of the first step is reacted with glycidyl methacrylate or allyl glycidyl ether.

The special technical feature of Invention I is that the hyperbranched polyester is produced by three steps. The special technical feature of Invention II is that two steps produce the hyperbranched polyester. Since the third step in Invention I, the esterification of the free hydroxyl groups, has been omitted in Invention II, the produced hyperbranched polymers in the two inventions are not the same. Inventions I-II are thus not so linked as to form a general inventive concept. There is no technical relationship among those inventions involving one or more of the same or corresponding technical features.

INTERNATIONAL SEARCH REPORT
Information on patent family members

08/05/00

International application No.
PCT/FI 00/00288

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9607688 A1	14/03/96	AT 187467 T	15/12/99
		AU 704344 B	22/04/99
		AU 3489395 A	27/03/96
		CA 2198755 A	14/03/96
		DE 69513840 D	00/00/00
		EP 0779908 A,B	25/06/97
		SE 0779908 T3	
		JP 10505377 T	26/05/98
		NO 971061 A	30/04/97
		SE 503559 C	08/07/96
		SE 9402994 A	09/03/96
		US 5834118 A	10/11/98
FI 923817 A	27/02/94	NONE	